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(54) TWO-PACKAGE COMPOSITIONS COMPRISING ADDITION INTER-POLYMERS AND POLYEPOXIDES

(71) We, PPG INDUSTRIES, INC. a corporation organised and existing under the laws of the State of Pennsylvania United States of America, of One Gateway Center, Pittsburgy, State of Pennsylvania 15222, United States of America, (Assignees of KARL FRANCIS SCHIMMEL, JAMES ANTHONY CLAAR, JEROME ALLAN SEINER, MARCO WISMER and WEN-HSUAN CHANG & ROGER MORRIS CHRISTENSON), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention relates to two-package compositions comprising addition interpolymers and polyepoxides.

Certain water-thinnable coating compositions composed of acidified addition copolymers containing pendent carboxyl groups and pendent aminoester groups formed by aminoethylating pendent carboxyl groups with an excess of alkylenimine and epoxy resins are known, as shown by U.S. Patent No. 3,719,629 to Martin et al, issued March 6, 1973. These acidified copolymers are cationic acid salts, i.e., the salt groups are provided by reacting basic groups with an acid. This creates a number of serious disadvantages. For example, because of the cationic nature of the copolymer, it cannot be readily formulated into a coating composition by blending it with the conventional anionic modifiers normally employed in coating compositions, acid sensitive pigments such as the carbonates cannot readily be employed, and the conventional anionic pigment dispersants cannot be utilized in the usual manner. Another disadvantage, due to the fact that the copolymer product is an acid salt, is that it cannot be satisfactorily employed as a coating material for unprimed metal substrates since such acid salts usually cause flash rusting.

Water-based coating compositions containing basic salts of polycarboxylic acid resins containing amine groups formed by iminating a portion of the carboxyl groups are shown by U.S. Patent No. 3,494,847, issue to Yurcheson et al on February 10, 1970. The coating compositions disclosed in U.S. Patent No. 3,494,847 generally utilize as the polycarboxylic acid resin certain fatty acid adducts containing unsaturation for curing, but in some cases interpolymers of acrylic and other vinyl monomers, at least one of which contains a hydroxyl group, are contemplated. In such cases, the interpolymer is cured with an amine-aldehyde condensate to which may be added a polyepoxide.

U.S. Patent No. 3,945,963, issued to Levine et al on March 23, 1976, described emulsions of acrylic interpolymers in combination with certain resins derived from epoxides. These resins are either very high molecular weight (abovc 20,000) or defunctionalized (and thus not a polyepoxide) by reaction of the epoxy groups, such high molecular weight or defunctionalization being necessary in order to provide the one-package compositions contemplated.

In accordance with this invention, two-package polymeric compositions are provided which, when inter-reacted, form crosslinked, hard, solvent-resistant and extremely stain-resistant materials. The film-forming components of these polymeric compositions consist essentially of a polyepoxide and an addition interpolymer containing a polymeric backbone

of two or more ethylenically unsaturated monomers, at least one of which contains carboxyl groups, pendent amine groups formed by reacting part of the carboxyl groups with an alkylenimine, and pendent salt groups formed by reacting part of the carboxyl groups with a base. There may or may not remain unreacted carboxyl groups, but in any event the number of salt groups should be sufficient to provide the desired viscosity and solubility characteristics. Usually the composition is intended to be dissolved or dispersed in water, and in such water-reducible systems the addition interpolymer should be sufficiently neutralized so as to have a pH, in aqueous medium, greater than about 6 and preferably greater than 7. The stability of admixed compositions is enhanced by employing an alkali metal hydroxide or a sterically-hindered tertiary amine to form the salt groups of the addition interpolymer.

These compositions can be made to be water-reducible, if desired, and in the preferred embodiments of the invention either or both of the film-forming vehicle components are in a solvent medium composed predominantly of water. When a water-reducible composition is desired, any organic solvents present should be miscible (in the proportion present) with water.

The polymeric compositions of the invention form cured products having excellent stain and solvent resistance which are useful in various coating, casting and molding applications and which are particularly useful as protective and decorative coatings.

A wide variety of polyepoxides may be utilized in the compositions of this invention, but in order to provide the cured products desired, the polyepoxide should have a 1,2-epoxy equivalence greater than 1.0, that is, in which the average number of 1,2-epoxy groups per molecule is greater than 1, and be of low molecular weight, i.e., below about 4000. The polyepoxide can be any of the well-known epoxides, such as, for example, those described in U.S. Patents Nos. 2,467,171; 2,615,007; 2,716,123; 3,030,336; 3,053,855 and 3,075,999. A useful class of polyepoxides are the polyglycidyl ethers of polyphenols, such as Bisphenol A, produced, for example, by etherification of a polyphenol with epichlorohydrin or dichlorohydrin in the presence of an alkali. The phenolic compound may be bis(4-hydroxyphenol)- 2,2-propane, 4,4'-dihydroxybenzophenone, bis(4-hydroxyphenyl)1,1-ethane, bis(4-hydroxyphenyl)1,1- isobutane; bis(4-hydroxy- tertiary-butyl-phenyl)2,2-propane, bis(2-hydroxynaphthyl)methane, 1,5-dihydroxy- naphthalene, or the like. Another quite useful class of polyepoxides are produced similarly from Novolak resins or similar polyphenol resins.

Also suitable are the similar polyglycidyl ethers of polyhydric alcohols which may be derived from such polyhydric alcohols as ethylene glycol, diethylene glycol, triethylene glycol, 1,2-propylene glycol, 1,4-butylene glycol, 1,5-pentanediol, 1,2,6-hexanetriol, glycerol, bis(4-hydroxycyclohexy)- 2,2-propane, and the like.

There can also be used polyglycidyl esters of polycarboxylic acids which are produced by the reaction of epichlorohydrin or a similar epoxy compound with an aliphatic or aromatic polycarboxylic acid, such as oxalic acid, succinic acid, gluratic acid, terephthalic acid, 2,6-naphthylene dicarboxylic acid, dimerized linolenic acid and the like. Examples are diglycidyl adipate and diglycidyl phthalate.

In addition, polyepoxides derived from the epoxidation of an olefinically unsaturated alicyclic compound may also be employed. Included are diepoxides comprising in part one or more monoepoxides. These polyepoxides are non-phenolic and are obtained by epoxidation of alicyclic olefins, for example, by oxygen and selected metal catalysts, by perbenzoic acid, by acetaldehyde monoperacetate, or by peracetic acid. Among such polyepoxides are the epoxyalicyclic ethers and esters, which are well known in the art.

Another class of polyepoxides which may be employed are those containing oxyalkylene groups in the epoxy molecule. Polyepoxides containing oxyalkylene groups can be produced by reacting some of the epoxy groups of a polyepoxide, such as the polyepoxides mentioned above, with a monohydric alcohol containing oxyalkylene groups.

Other epoxy-containing compounds and resins which may be employed include nitrogeneous diepoxides such as disclosed in U.S. Patent No. 3,365,471; epoxy resins from 1,1-methylene bis(5- substituted hydantoin), U.S. Patent No. 3,391,097; bis-imide containing diepoxides, U.S. Patent No. 3,450,711; heteocyclic N,N'-diglycidyl compounds, U.S. Patent No. 3,503,979; amino epoxyphosphonates, British Patent No. 1,172,916; 1,3,5-triglycidyl isocyanurates, and the like.

In some instances, chain-extended polyepoxide adducts may be employed to impart a desired property to films formed from the compositions of the invention, such as, for example, flexibility. Such adducts can be prepared by reacting a polyepoxide, such as, for instance, the polyglycidyl ethers of polyphenols described above, with an organic polyol having at least two alcoholic primary hydroxyls at temperatures of from about 120°C. to about 200°C. in the presence of a suitable catalyst. Various organic polyols may be utilized in the chain-extension reactions. An especially useful class of organic polyols are the various polyethylene glycols marketed under the designation Carbowax. Other organic polyols which

may be utilized include low molecular weight diols, triols and higher polymeric polyols such as polyester polyols, polyester polyols and the like. Of these, the polyester polyols, particularly the polycaprolactone polyols, such as those described in U.S. Patent No. 3,169,945 to Hostettler, are especially useful.

It should be noted that while such chain-extended polyepoxide adducts can impart desirable properties to films formed from the compositions herein, they may also adversely affect other properties such as stain resistance. Accordingly, in applications where extremely high levels of stain resistance are required, only minor amounts of such chain-extended polyepoxide adducts should be utilized. In such cases, it is preferred to limit the amount of such adducts to 40 percent by weight or less of the total poyepoxide component employed in the polymeric composition.

The amounts of polyepoxide included in the compositions of the invention should be sufficient to provide a crosslinked product upon inter-reaction with the addition polymer but may vary considerably, depending upon desired properties. Usually from about 5 to about 95 percent by weight of the epoxy resin, based upon the combined weight solids of the addition copolymer and epoxy resin may be employed, with a preferred amount being from about 25 to about 75 percent by weight.

As indicated above, the other essential component of the water-reducible polymeric compositions of the invention is an addition interpolymer containing carboxyl groups, at least part of which are reacted with an alkylenimine and part with another base, as discussed herein. The addition interpolymer component is generally prepared by reacting an addition interpolymer containing carboxyl groups with an alkylenimine in sufficient amount to iminate a portion of the carboxyl groups and then with a base to neutralize at least a portion of the remaining carboxyl groups. The order of reaction is not usually critical.

The term "iminate" as employed throughout this specification means to react an imine (i.e., an alkylenimine or substituted alkylenimine) with a carboxyl group. Thus, an iminated interpolymer refers to an interpolymer in which the carboxyl groups thereof have been reacted or partially reacted with an imine.

The addition interpolymer containing carboxyl groups is prepared by interpolymerizing at least one polymerizable ethylenically unsaturated carboxylic acid monomer with one or more other polymerizable ethylenically unsaturated monomers utilizing conventional vinyl addition solution polymerization techniques and procedures. Thus, the monomer mixture is ordinarily polymerized in a solvent medium and in the presence of a suitable catalyst, usually under controlled elevated temperatures with agitation until the polymerization reaction is complete. Various modifications commonly practiced in solution polymerization reactions, such as stepwise addition of the monomer mixture during polymerization, incremental addition of catalyst, polymerization under an inert atmosphere, continuous or batch polymerization and the like may be employed.

Ethylenically unsaturated carboxylic acids which may be employed in forming the interpolymer include alpha, beta-ethylenically unsaturated monocarboxylic acids such as acrylic acid, methacrylic acid, cinnamic acid, and the like; unsaturated dicarboxylic acids such as maleic acid, fumaric acid, itaconic acid and the like; and half esters of unsaturated dicarboxylic acids such as t-butyl hydrogen maleate, isopropyl hydrogen fumarate and the like. It should be noted that when acids are referred to above, the anhydrides of such acids, where they exist, may also be utilized. In addition, mixtures of the foregoing acids (or anhydrides) may be employed. The preferred ethylenically unsaturated carboxylic acids herein are the alpha, beta-ethylenically unsaturated monocarboxylic acids and of these acrylic and methacrylic acids are especially preferred.

The unsaturated carboxylic acid monomer comprises usually from about 5 to about 60, preferably from 10 to 50, percent by weight of the addition interpolymer.

The other monomer or monomers which may be employed in forming the interpolymer include essentially any copolymerizable monomer. Examples are esters of unsaturated acids such as those mentioned above, especially alkyl acrylates and methacrylates; unsaturated esters of organic and inorganic acids, such as vinyl halides, vinylidene halides, vinyl acetate, dialkyl maleates, allyl chloride and the like; monoolefinic and diolefinic hydrocarbons such as styrene, alpha-methyl styrene, the halo-substituted styrenes, vinyl toluene, vinyl naphthalene, allyl alcohol, 1,3-butadiene, 2-chlorobutene, isoprene and the like; unsaturated amides (unsubstituted or substituted) such as acrylamide, methacrylamide, diacetone acrylamide, crotonamide, N-(methoxymethyl)acrylamide, N-(propoxymethyl)acrylamide, N-(butoxymethyl)acrylamide, N-(butoxymethyl)methacrylamide, N-methylol acrylamide and the like; and unsaturated nitriles such as acrylonitrile, methacrylonitrile and the like. The specific monomers chosen and their proportions will depend upon the properties desired and their reactivity with each other and the acid monomer, using considerations well known in the art.

Particularly preferred monomers reacted with the ethylenically unsaturated carboxylic

acids to form the interpolymer are polymerizable ethylenically unsaturated aminolysis-resistant organic monomers. It has been found storage stability problems involved in amine group-containing interpolymers are at lest to a major extent caused by internal aminolysis reactions. Aminolysis occurs as the result of a reaction between a primary or secondary amine group and an ester group thereby resulting in the formation of an amide. In the case of amine group-containing additon interpolymers, it is believed that the aminolysis reaction occurs between the pendent amine groups formed by imination of pendent carboxyl groups and pendent ester groups formed from, for example, the esters of acrylic and methacrylic acid. The aminolysis reaction in such interpolymers is believed to proceed by a mechanism in which the pendent amine groups of one polymer chain react with the pendent ester groups of another polymer chain resulting in the formation of an amide and causing crosslinking between the polymer chains. This, in turn, can lead to an increase in molecular weight of the copolymer and eventual gellation. The term "aminolysis-resistant" as used throughout this specification refers to organic groups which resist or impede the formation of amide groups.

It has been found the storage stability (prior to mixing with the polyepoxide) of the herein amine group-containing interpolymer is greatly improved by incorporating certain aminolysis-resistant organic monomers into the here described interpolymers. Polymerizable ethylenically unsaturated aminolysis-resistant organic monomers which are employed in forming the interpolymer include certain monoolefinic and diolefinic hydrocarbons, unsaturated carboxylic acid amides (substituted or unsubstituted), unsaturate organonitriles and certain esters of alpha, alkyl-substituted carboxylic acids. Mixtures of such aminolysis-resistant organic monomers can also be utilized. The preferred aminolysis-resistant organic monomers are certain esters of alpha, alkyl-substituted carboxylic acids.

Aminolysis-resistant monoolefinic and diolefinic hydrocarbon monomers, which can be employed include styrene, alpha-methyl styrene, the halo-substituted styrenes, vinyl toluene, vinyl naphthalene, allyl alcohol, butadiene, isoprene and similar compounds. The preferred aminolysis-resistant hyrocarbon monomers are the vinyl aromatic hydrocarbons and of these, styrene, alpha-methyl styrene and vinyl toluene are especially preferred.

Aminolysis-resistant unsaturated carboxylic acid amides which can be employed include both unsubstituted and substituted amides. Thus, there can be employed unsubstituted amides such as acrylamide, methacrylamide, crotonamide and the like; N-alkoxyalkyl-substituted amides such as N-(methoxymethyl) acrylamide, N-(propoxymethyl) acrylamide, N-(isopropoxymethyl) acrylamide, N-(butoxymethyl) acrylamide, N-(butoxymethyl) methacrylamide and the like; and methylolated amides such as N-methylolacrylamide and the like. Mixtures of such amides may also be utilized. The preferred aminolysis-resistant amides are the N-alkoxyalkyl- substituted amides and of these, N-(butoxymethyl) acrylamide is especially preferred.

Still other aminolysis-resistant monomers which can be useful include unsaturated organonitriles such as acrylonitrile, methacrylonitrile and the like.

As indicated above, the preferred ethylenically unsaturated aminolysis-resistant organic monomers for use in forming the interpolymers of this invention are certain non-methyl esters of alpha, alkyl-substituted carboxylic acids. These aminolysis-resistant esters include ethyl methacrylate, propyl methacrylate, butyl methacrylate and the like; preferred are branched chain and alicyclic esters of methacrylic acid, such as isobutyl methacrylate, tertiary butyl methacrylate, isobornyl methacrylate and cyclohexyl methacrylate. Mixtures of such monomers can also be utilized. An especially preferred aminolysis-resistant ester is isobutyl methacrylate.

If desired, virtually any of the organic solvents heretofore employed in preparing acrylic interpolymers of this kind may be utilized as the solvent medium in preparing the addition interpolymer. Thus, alcohols such as propanol, butanol, or other lower alkanols; ketones such as methyl ethyl ketone, methyl n-butyl ketone, and the like; and aromatic hydrocarbons such as xylene, toluene and the like as well as mixtures of such solvents may be employed. When, as in the preferred embodiments, the ultimate interpolymer product is intended to be dissolved in or thinned with water, it is preferred to employ water-soluble or water-miscible organic solvents as the solvent medium in the polymerization reaction. Suitable solvents of this type include ether type alcohols, such as, for example, ethylene glycol monobutyl ether, ethylene glycol monoethyl ether, diethylene glycol monoethyl ether, glycol monomethyl ether, dipropylene glycol monomethyl ether, and the like; and lower alkanols having 2 to 4 carbon atoms such as ethanol, propanol, isopropanol, butanol, and the like, or mixtures of these solvents. Mixtures of the above water-solule or water-miscible organic solvents and water can also be advantageously used as the solvent medium in the polymerization reaction.

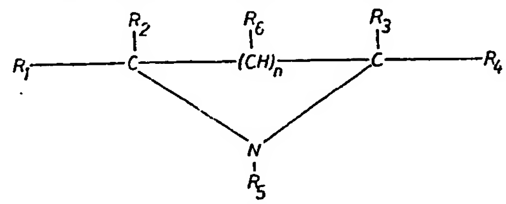
In the polymerization of the monomers, the polymerization temperature employed can vary considerably, depending on the specific monomers employed, the use of catalysts and other conditions. Usually a vinyl polymerization catalyst is used, the preferred catalysts being azo compounds such as, for example, alpha, alpha'-azobisisobutyronitrile and peroxides such

as benzoyl eproxide, cumene hydroperoxide and tertiary butyl perbenzoate. The quantity of catalyst employed may be varied considerably, however, in most instances it is desirable to utilize from about 0.1 to about 3.0 percent by weight based on monomer solids.

If interpolymers of relatively low molecular weight are desired, a chain-modifying agent or chain transfer agent is ordinarily added to the polymerization mixture. The mercaptans, such as dodecyl mercaptan, tertiary dodecyl mercaptan, octyl mercaptan, hexyl mercaptan, and the like, are conventionally used for this purpose. In addition, mercapto-esters, such as isooctyl thioglycolate can advantageously be used. Other chain transfer agents which may be employed in some instances include cyclopentadiene, allyl carbamate, alpha-methyl styrene, alpha-methyl styrene dimers and the like.

The iminated interpolymers are prepared by reacting the addition interpolymer containing carboxyl groups with an alkylenimine in sufficient amount to iminate a portion of the carboxyl groups, thereby producing a product containing carboxyl groups and pendent amine groups. The amount of alkylenimine employed in the imination reaction can be varied considerably, depending on the desired properties and the proportion of acid monomer moieties in the addition interpolymer. In general, an amount of alkylenimine sufficient to iminate from about 5 mole percent to about 95 mole percent of the carboxylic acid groups of the interpolymer may be employed. However, it is preferred in this invention to iminate at least about 15 mole percent of the carboxylic acid groups and usually not more than about 50 mole percent is iminated.

Alkylenimines (which term includes substituted alkylenimines) which may be employed in the imination reaction includes imines such as those of the formula:



where R_1, R_2, R_3, R_4 and R_5 are each hydrogen; alkyl, such as methyl, ethyl, propyl, or the like, having, for example, up to about 20 carbon atoms; aryl such as phenyl or the like; alkaryl, such as tolyl, xylyl or the like; or aralkyl, such as benzyl, phenethyl, or the like. R_6 in the formula above is hydrogen or a lower alkyl radical, usually having not more than about 6 carbon atoms and n is an integer from 0 to 1, preferably 0. Substituted radicals of the classes indicated are included where the substituent groups do not adversely affect the basic nature of the imine in the reaction. Such substituents may include groups such as cyano, halo, amino, hydroxy, alkoxy and carbalkoxy. The substituted groups may thus be cyanoalkyl, haloalkyl, aminoalkyl, hydroxyalkyl, alkoxyalkyl, carbalkoxyalkyl and similar substituted derivatives of aryl, alkaryl and aralkyl groups where present.

It will be recognized by those skilled in the art that compounds containing certain combinations of the above groups cannot be obtained, for example, because of factors such as steric hindrance or intra-molecular interaction. For this reason, in most of the compounds of the class described, several of the groups designated by R_1 through R_6 represent hydrogen. However, the efficacy of the various alkylenimines (whether or not within the above formula) does not depend upont he particular nature of any of the substituents, but rather the imine linkage.

Illustrative examples of suitable alkylenimines (i.e., aziridines) falling within the scope of the above formula include ethylenimine (aziridine), 1,2-propylenimine (2-methyl aziridine), 1,3-propylenimine (azetidine), 1,2-dodccylenimine (2-decyl aziridine), 1,1-dimethyl ethylenimine (2,2-dimethyl aziridine), phenyl ethylenimine (2-phenyl aziridine), tolyl ethylenimine [2-(4-methylphenyl)aziridine], benzyl ethylenimine (2-phenylmethyl aziridine), 1,2-diphenyl ethylenimine (2,3-diphenyl aziridine), hydroxyethyl ethylenimine [2-(2-hydroxyethyl)aziridine], aminoethyl ethylenimine [2-(2-aminoetyl)aziridine], 2-methyl propylenimine (2-methyl azetidine), 3-chloropropyl ethylenimine [2-(3-chloropropyl)aziridine], p-chlorophenyl ethylenimine [2-(4-chlorophenyl)aziridine], methoxyethyl ethylenimine [2-(2-methoxyethyl)aziridine], dodecyl aziridinyl formate (dodecyl 1-aziridinyl carboxylate), N-ethyl ethylenimine (1-ethyl aziridine), N-butyl ethylenimine (1-butyl aziridine), N-(2-hyroxyethyl)ethylenimine [1-(2-hydroxyethyl)aziridine] and the like.

Because of their availability and because they have been found to be among the most effective, the preferred imines are alkylenimines having 2 to 4 carbon atoms, and especially ethylenimine, 1,2-propylenimine and N-hydroxyethyl ethlenimine.

The salt of the addition interpolymers herein is obtained by neutralizing at least a portion

of the carboxyl groups of the addition interpolymer with a sufficient amount of a basic compound to produce an addition interpolymer salt having after reaction with the desired amount of alkylenimine, the desired level of neutralization. The amount of base employed for that purpose may vary considerably, depending upon factors such as the amount of acid included in the interpolymer, the type of base utilized, the identity and amount of alkylenimine used, and so forth. The specific amount and type of base utilized is selected such that after neutralization, the product has the desired viscosity solubility and other characteristics. Usually the level of neutralization is such that the addition interpolymer salt product has a pH of greater than about 6 and, preferably, greater than 7.0 in the presence of water.

The reaction with the base is usually carried out after imination but may be partly or wholly carried out prior to imination or simultaneously therewith.

Various basic compounds may be employed in the neutralization procedure, including inorganic bases such as the alkali metal hydroxides and organic bases such as ammonia or amines. Thus, alkali metal hydroxides such as potassium hyroxide, sodium hydroxide and the like may be employed. In general, the amines employed in the neutralization procedure may be any of the amines used for solubilizing resin systems known heretofore, including ethylamine, butylamine, dimethylamine, cyclohexylamine, morpholine, monoethanolamine, diethanolamine, dimethylethanolamine, diethylethanolamine, and the like.

While any of the aforementioned basic compounds can be employed in forming the pendent salt groups of the interpolymer, the preferred basic compounds in certain instances are sterically-hindered tertiary amines having the structure:

$$R_1 - \underset{|}{\overset{R_2}{\overset{|}{N}}} - R_3$$

wherein R_1, R_2 and R_3 are each aliphatic or cycloaliphatic radicals having from 2 to 10 carbon atoms. The use of the sterically-hindered tertiary amines to form the salt groups is preferred due to the fact the stability of the mixed compositions, i.e., the polyepoxide and the interpolymer, is lengthened. Illustrative of the particularly preferred sterically-hindered tertiary amines which are employed are diethylethanolamine, N-ethyl morpholine, triethylamine, triethanolamine, diisopropylethanolamine, triisopropanolamine, tripropylamine and ethyldiethanolamine. The specified preferred amine is diethylethanolamine.

The proportions of polyepoxide and addition interpolymer salt included in two-package compositions of the invention may vary considerably, depending on desired properties of the final cured product intended to be formed therefrom. In general, from about 5 to about 95 percent by weight of the addition interpolymer salt, based upon the combined weight solids of the addition interpolymer salt and polyepoxide may be employed with a preferred amount being from about 25 to about 75 percent by weight.

In addition to the polyepoxide and the addition interpolymer salt, the compositions of the invention may contain (as non-essential components) various other additives, including pigments and dyes of the type ordinarily utilized, fillers, plasticizers, anti-oxidants, flow control agents, surfactants, thickeners and other such formulating additives.

The compositions of the invention may be employed in various applications but are especially useful in coating applications requiring a high level of stain and solvent resistance. Thus, for example, the compositions herein are especially useful as coatings for hospital walls, operating rooms and the like.

The compositions herein can be applied by any conventional method, including brushing, rolling, dipping, flow coating, roll coatings, spraying and the like. Conventional spray techniques and equipment can be utilized.

The polymeric compositions of the invention may be cured by baking at moderate or elevated temperatures, if desired. However, one especially advantageous property of the curable compositions is that they can be cured by permitting them to dry (i.e., the solvent to evaporate) in air at ambient temperature without the use of heat, whereupon they inter-react to form a crosslinked product. As will be evident, ambient temperature curable compositions are of considerable advantage in that they provide for significant energy savings in comparison to compositions which require elevated temperature for curing.

In the following Examples, Examples 1 to 6 and 14 to 17 illustrate the invention and Examples 7 to 13 illustrate addition interpolymers which may be used in the invention. All parts and percentages in the examples and throughout the specification are by weight unless otherwise indicated.

EXAMPLE 1

(a) Preparation of the Amino-Acrylic Interpolymer Package

The amino-acrylic addition interpolymer component of the package was prepared as follows:

Into a reactor equipped with a stirrer, thermometer, nitrogen inlet, dropping funnel and a condenser fitted with a water trap was charged 800 grams of ethylene glycol monoethyl ether (hereinafter ethyl Cellosolve - "CELLOSOLVE" is a registered Trade Mark). The contents of the reactor were heated to reflux and then a mixture consisting of 156.9 grams of styrene, 235.0 grams of methyl methacrylate, 156.9 grams of ethyl acrylate, 235.4 grams of methacrylic acid, 15.7 grams of tertiary dodecyl mercaptan, 100.0 grams of ethyl Cellosolve and 12.0 grams of benzoyl peroxide was charged to the reactor over a period of approximately 2.5 hours. (Based on monomer solids, the monomer charge consisted of 20 percent styrene, 30 percent methyl methacrylate, 20 percent ethyl acrylate, and 30 percent methacrylic acid.) The reaction mixture was then held for one hour at reflux. Following the hold period, 3 grams of benzoyl peroxide and 100 grams of ethyl Cellosolve were added to the reactor over a period of about 30 minutes and the reaction mixture then held for one hour at reflux. The reaction mixture was then cooled to about 25°C. and 93.9 grams of propylenimine were added to the reactor.

An exotherm was noted during the addition of propylenimine and the temperature was held at between 45-55°C. with cooling. After the addition of propylenimine was completed, the reaction mixture was held for one hour at 55-60°C. Following this hold period, 90.8 grams of dimethyl ethanolamine were added to the reactor and the temperature held at 50-55°C. for about 30 minutes.

The resultant addition interpolymer solution had the following properties:

Solids content at 150°C.	47.0 percent
Gardner-Holdt viscosity	Z7
Gardner color	2^+
Amine equivalent weight (based on propylenimine)	1213.8

The finished amino-acrylic interpolymer package was then prepared by admixing the following ingredients utilizing conventional paint mixing techniques:

	Parts by Weight
Amino-acrylic interpolymer above	300.0
TiO_2	125.0
Triton+ X-45 (non-ionic surfactant)*	10.0
Strodex SEK-50 (anionic surfactant)**	10.0
Propylene glycol	25.0
Ethyl Cellosolve	40.0
Water	5.0

\+ "TRITON" is a registered Trade Mark

* A non-ionic surfactant consisting of an ethoxylated alkyl phenol prepared from about 4.5 moles of ethylene oxide, available from Rohm & Haas Company.

** A potassium salt of an alkyl phosphate ester available from Dexter Chemical Company.

(b) Preparation of the Polyepoxide Package

A pigmented polyepoxide emulsion was prepared by admixing the following ingredients utilizing concentional emulsion preparation and paint mixing techniques:

	Parts by Weight
Epon 828*	40.0
Epon 834** (90% solution in xylene)	260.0
TiO_2	250.0
Magnesium silicate	75.0
Igepal CO897 (non-ionic surfactant)(1)	35.0
Triton X-100 (non-ionic surfactant)(2)	10.0
Atlas+ G3300 (anionic surfactant)(3)	5.0

Nopco+ NDW (anti-foaming agent)(4)	4.0
Strodex SEK-50 (anionic surfactant)(5)	2.0
Water	429.5

+ "ATLAS" and "NOPCO" are registered Trade Marks

* An epoxy resin of epichlorohydrin-Bisphenol A having an epoxide equivalent of 185-192 and a viscosity as measured by ASTM D-445 of 100-160 poises, available from Shell Chemical Company.

** An epoxy resin of epichlorohydrin-Bisphenol A having an epoxide equivalent of 230-280 and a Gardner-Holdt viscosity of O-V, available from Shell Chemical Company.

(1) A non-ionic surfactant consisting of an ethoxylated alkyl phenol prepared from about 30 moles of ethylene oxide, available from GAF Corporation.

(2) A non-ionic surfactant consisting of an ethoxylated alkyl phenol prepared from about 9.5-10 moles of ethylene oxide, available from Rohm and Haas Company.

(3) An anionic surfactant available from Atlas Chemical Company.

(4) An anti-foaming agent available from Nopco Division, Diamond Shamrock.

(5) An anionic surfactant consisting of a potassium salt of an alkyl phosphate ester available from Dexter Chemical Company.

A polymeric coating composition was prepared by blending the above amino-acrylate and polyepoxide packages 1:1 on a volume basis. The resulting polymeric coating composition was drawn down on duplicate metal panels using a 3-mil Bird Bar. The coated panels were then cured by permitting the panels to air dry at ambient temperature for 8 hours and then placing the panels in a 140°F. oven for an additional 16 hours.

The cure and solvent resistance of the coating was then evaluated utilizing a standard solvent resistance test in which the cloth impregnated with an organic solvent is rubbed across the surface of the film and the number of rubs passed before the film is removed from the substrate is reported. The coating of this example passed over 200 acetone double rubs in one test and over 300 ethanol double rubs in another test without film loss or softening indicating excellent cure and solvent resistance.

The stain resistance of a coating formed from the polymeric composition of this example was evaluated using a conventional stain resistance test employed in the coating industry. In this example, the resistance of the coating to staining from merthiolate was evaluated by applying a line of merthiolate across the top of a panel in which the coating was cured as indicated above. The panel containing the applied merthiolate was permitted to age for 16 hours and then an attempt was made to remove the applied line of merthiolate with solvents such as soap and water, Mr. Clean and mineral spirits. The line of merthiolate was readily removed with any of the above solvents, indicating that the cured coating of this example has excellent resistance to staining by merthiolate.

EXAMPLE 2

(a) Preparation of the Amino-Acrylic Interpolymer Package

An amino-acrylic interpolymer package was prepared by mixing the following ingredients, utilizing the procedure of Example 1:

	Parts by Weight
Amino-acrylic interpolymer of Ex. 1	300.0
TiO_2	125.0
Triton X-45 (non-ionic surfactant)	10.0
Potassium tripolyphosphate (50% solution in water)	10.0
Propylene glycol	25.0
Ethyl Cellosolve	40.0
Water	5.0

(b) Preparation of the Polyepoxide Package

In this example, the pigmented polyepoxide emulsion of Example 1 was utilized as the polyepoxide package.

A polymeric coating composition was prepared by blending the above amino-acrylic interpolymer and polyepoxide packages 1:1 on a volume basis as in Example 1. The resulting

polymeric coating composition was applied to metal panels, cured and evaluated for solvent and stain resistance as in Example 1.

The cured coating passed over 200 ethanol double rubs, indicating excellent cure and solvent resistance. In addition, cured coatings formed from the composition of this example exhibited excellent resistance to merthiolate staining.

EXAMPLE 3

(a) Preparation of the Amino-Acrylic Interpolymer Package

An amino-acrylic interpolymer package was prepared by admixing the following ingredients, utilizing the procedure of Example 1:

	Parts by Weight
Amino-acrylic interpolymer of Ex. 1	300.0
TiO_2	125.0
Triton X-45 (non-ionic surfactant)	10.0
Tamol 731 (anionic surfactant)*	10.0
Propylene glycol	25.0
Ethyl Cellosolve	40.0
Water	5.0

* An anionic surfactant consisting of the sodium salt of a polycarboxylic acid, available from Rohm and Haas Co.

(b) Preparation of the Polyepoxide Package

In this example,the pigmented polyepoxide emulsion of Example 1 was utilized as the polyepoxide package.

A polymeric coating composition was prepared by blending the above amino-acrylic interpolymer and polyepoxide packages 1:1 on a volume basis as in Example 1. The resulting polymeric coating composition was applied to metal panels, cured and evaluated for solvent and stain resistance, as in Example 1.

The cured coating passed over 200 acetone double rubs and over 200 ethanol double rubs, indicating excellent cure and solvent resistance. In addition, cured coatings formed from the composition of this example exhibited excellent resistance to merthiolate staining.

EXAMPLE 4

(a) Preparation of the Amino-Acrylic Interpolymer Package

An amino-acrlic interpolymer package was prepared by admixing the following ingredients, utilizing the procedure of Example 1:

	Parts by Weight
Amino-acrylic interpolymer of Ex. 1	300.0
TiO_2	125.0
Igepal CO 897 (non-ionic surfactant)	3.0
Triton X-100 (non-ionic surfactant)	2.0
Propylene glycol	25.0
Ethyl Cellosolve	40.0
Water	5.0

(b) Preparation of the Polyepoxide Package

In this example, the pigmented polyepoxide emulsion of Example 1 was utilized as the polyepoxide package.

A polymeric coating composition was prepared by blending the above amino-acrylic interpolymer and polyepoxide packages 1:1 on a volume basis as in Example 1. The resulting polymer coating composition was applied to metal panels, cured and evaluated for solvent and stain resistance as in Example 1.

The cured coating passed over 200 acetone double rubs and over 200 ethanol double

rubs, indicating excellent cure and solvent resistance. In addition, cured coatings formed from the composition of this example exhibited excellent resistance to merthiolate staining.

EXAMPLE 5

(a) Preparation of the Amino-Acrylic Addition Interpolymer Package

The amino-acrylic addition interpolymer component of the package was prepared as follows:

Into a reactor equipped with a stirrer, thermometer, nitrogen inlet, dropping funnel and a condenser fitted with a water trap was charged 896.0 grams of ethyl Cellosolve. The contents of the reactor were heated to 133°C. and a mixture consisting of 267.8 grams of styrene, 232.2 grams of methacrylic acid, 250.0 grams of butyl acrylate, 250.0 grams of 2-ethylhexyl acrylate, 179.3 grams of ethyl Cellosolve, and 32.0 grams of tertiary butyl peracetate was added over a 2 hour period. (Based on monomer solids, the monomer charge consisted of 26.8 percent styrene, 23.3 percent methacrylic acid, 25.0 percent butyl acrylate and 25.0 percent 2-ethylhexyl acrylate). Following this addition, 8.0 grams of tertiary butyl peracetate and 44.8 grams of ethyl Cellosolve were added to the reactor over a 35 minute period. Then the contents of the reactor were cooled to about 33°C. and 71.8 grams of propylenimine were added to the reaction mixture. After the propylenimine addition was completed, 85.7 grams of potassium hydroxide was added to the reaction mixture, following which 100.0 grams of water were added.

The resultant addition interpolymer solution had the following properties:

Solids content at 150°C.	47.8 percent
Gardner-Holdt viscosity	U-V
Amine equivalent weight	1919

The finished amino-acrylic interpolymer package was then prepared by admixing the following ingredients utilizing conventional paint mixing techniques:

	Parts by Weight
Amino-acrylic interpolymer above	300.0
TiO_2	125.0
Igepal CO 897 (non-ionic surfactant)	5.0
Triton X-100 (non-ionic surfactant)	2.0
Strodex SEK 50 (anionic surfactant)	5.0
Propylene glycol	25.0
Ethyl Cellosolve	30.0
Water	20.0

(b) Preparation of the Polyepoxide Package

In this example, the pigmented polyepoxide emulsion of Example 1 was utilized as the polyepoxide package.

A polymeric coating composition was prepared by blending the above amino-acrylic interpolymer and polyepoxide packages 1:1 on a volume basis as in Example 1. The resulting polymeric coating composition was applied to metal panels, cured and evaluated for solvent and stain resistance as in Example 1.

The cured coating passed over 200 acetone double rubs and over 200 ethanol double rubs, indicating excellent cure and solvent resistance. In addition, cured coatings formed from the composition of this example exhibited excellent resistance to merthiolate staining.

EXAMPLE 6

(a) Preparation of the Amino-Acrylic Addition Interpolymer Package

In this example, the amino-acrylic addition interpolymer package of Example 5 was utilized.

(b) Preparation of the Polyepoxide Package

In preparing the polyepoxide package, a polyepoxide adduct was first prepared in the

following manner:

To a 5 liter flask equipped with heating means, thermometer, and stirrer were charged 380.0 grams of Epon 828, 200.0 grams of Carbowax 400 (a waxy polyethylene glycol having a molecular weight of 400, a specific gravity of 1.1281 and a melting point of 4 to 8°C.), and 2.9 grams of $SnCl_2$. "CARBOWAX" is a registered Trade Mark. The mixture was heated to 180°C. and held at temperature until a sample of the reaction product thinned with butyl Cellosolve to a ratio of 75 percent reaction product and 25 percent butyl Cellosolve attained a Gardner-Holdt viscosity of J-K. The resultant polyepoxide adduct had an epoxide equivalent of 567 and, after aging over night, a Gardner-Holdt viscosity of R.

The finished polyepoxide package was then prepared by admixing the following ingredients utilizing conventional paint mixing techniques:

	Parts by Weight
Polyepoxide adduct above	283.0
Triton X-100 (non-ionic surfactant)	4.0
Nopco NDW (antifoaming agent)	4.0
Strodex SEK-50 (anionic surfactant)	2.0
Water	152.0

A polymeric coating composition was prepared by blending the above amino-acrylic interpolymer and polyepoxide packages 1:1 on a volume basis. The resultant polymeric coating composition was applied to metal panels, cured and evaluated for solvent and stain resistance as in Example 1.

The cured coating passed over 200 acetone double rubs and over 200 ethanol double rubs, indicating excellent cure and solvent resistance. Cured coatings formed from the composition of this example exhibited decreased resistance to staining. However, other evaluations in which the polyepoxide package of the composition consisted of blends of polyepoxides such as Epon 828 or Epon 834 with minor amounts of polyepoxide adducts of the above type showed much less decrease in stain resistance.

EXAMPLE 7

Into a reactor equipped as in Example 1 was charged 200.0 grams of dipropylene glycol monoethyl ether and 100.0 grams of propylene glycol monomethyl ether. The contents of the reactor were then heated to 123°C. and a solution consisting of 384.3 grams of isobutyl methacrylate, 164.9 grams of methacrylic acid, 16.5 grams of isooctyl thioglycolate, 31.3 grams of tertiary-butyl peracetate, 40.0 grams of dipropylene glycol monomethyl ether, and 20.0 grams of propylene glycol monomethyl ether was added to the reactor over a 2 hour period and the reaction mixture was then held for 1 hour. (Based on monomer solids, the monomer charge consists of 70 percent isobutyl methacrylate and 30 percent methacrylic acid.) Following the 1 hour hold period, 3.2 grams of tertiary-butyl peracetate, 8.4 grams of dipropylene glycol monomethyl ether and 4.3 grams of propylene glycol monoethyl ether were added over a period of 30 minutes followed by a 1 hour hold. Following this period, 120.0 grams of dipropylene glycol monomethyl ether and 60.0 grams of propylen glycol monomethyl ether were added to the reactor and the contents of the reactor were then cooled. Then 67.2 grams of diethylethanolamine were added followed by cooling. Following this addition, 32.5 grams of propylenimine were added at which point an exotherm was observed. The reaction mixture was then held for 2 hours at temperature. After this period, 67.2 grams of diethylethanolamine were added.

The resultant addition interpolymer had the following properties:

Solids content at 150°C.	50.8 per cent
Gardner-Holdt viscosity	Z_5-Z_6

The above interpolymer is water-thinnable and can also be thinned with an organic solvent such as ethyl Cellosolve.

EXAMPLE 8

Into a reactor equipped as in Example 1 was charged 305.1 grams of propylene glycol monomethyl ether. The contents of the flask were heated to 120°C. and a solution consisting of 288.6 grams of isobutyl methacrylate, 123.7 grams of methacrylic acid, 12.4 grams of isooctyl thioglycolate, 23.5 grams of tertiary-butyl peracetate and 90.0 grams of

propylene glycol monoethyl ether was added over a period of 2 hours. (Based on monomer solids, the monomer charge consists of 70 percent isobutyl methacrylate and 30 percent methacrylic acid.) After the addition was complete, the reaction mixture was held at temperature for 1 hour. Following this hold period, 2.4 grams of tertiary-butyl peracetate and 12.1 rams of propylene glycol monomethyl ether were added over a 30 minute period and the mixture then held at temperature for 1 hour. The reaction mixture was then cooled to 39°C. After cooling was completed, 37.5 grams of hydroxyethyl ethylenimine were added to the contents of the reactor at which time an exotherm was observed. The reaction mixture was permitted to exotherm and the mixture was held at temperature for 3 hours. Following this period, 102.0 grams of dietylethanolamine were added.

The resultant addition interpolymer had the following properties:

Solids content at 150°C.	54.0 percent
Gardner-Holdt viscosity	Z_6
Gardner color	3

The interpolymer of this example is water-thinnable and can also be thinned with an organic solvent such as ethyl Cellosolve.

EXAMPLE 9

Into a reactor equipped as in Example 1 was charged 1132.3 grams of propylene glycol monomethyl ether and 1132.4 grams of dipropylene glycol monomethyl ether. The contents of the reactor were heated to about 124°C. and a solution consisting of 2903.1 grams of isobutyl methacrylate, 1243.8 grams of methacrylic acid, 124.2 grams of isooctyl thioglycolate, 236.6 grams of tertiary butyl peracetate, 226.7 grams of propylene glycol monomethyl ether, and 226.7 grams of dipropylene glycol monomethyl ether was added over a two hour period. (Based on monomer solids, the monomer charge consists of 70 percent isobutyl methacrylate and 30 percent methacrylic acid.) The reaction mixture was then held at temperature for 1 hour. Following the hold period, 24.3 grams of tertiary butyl peracetate, 10.1 grams of propylene glycol monomethyl ether, and 10.1 grams of dipropylene glycol monoethyl ether were added to the reactor over a 30 minute period and the reactor mixtuer then held for 1 hour at temperature. After the hold period, 678.9 grams of propylene glycol monomethyl ether and 678.9 grams of dipropylene glycol monomethyl ether were added. Following this addition, 395.2 grams of diethylethanolamine were added to the reactor and the reaction mixture was then cooled. After cooling, 186.2 grams of ethylenimine were added and the mixture held for 2 hours. Following this hold period, 790.4 grams of diethylethanolamine were added to the reactor.

The resultant addition interpolymer had the following properties:

Solids content at 150°C.	52.4 percent
Gardner-Holdt viscosity	Z_6–Z_7
Gardner color	3

The interpolymer of this example is water-thinnable and can also be thinned with an organic solvent such as ethyl Cellosolve.

EXAMPLE 10

Into a reactor equipped as in Example 1 was charged 270.2 grams of propylene glycol monomethyl ether. The contents of the reactor were heated to 120°C. and a mixture consisting of 288.6 grams of cyclohexyl methacrylate, 123.7 grams of methacrylic acid, 12.4 grams of isooctyl thioglycolate, and 23.5 grams of tertiary-butyl peracetate was added over a 2 hour period. The reaction mixture was then held at temperature for 1 hour. (Based on monomer solids, the monomer charge consisted of 70 percent cyclohexyl methacrylate and 30 percent methacrylic acid.) After the hold period, 2.4 grams of tertiary-butyl peracetate and 12.1 grams of propylene glycol monomethyl ether were added to the reactor over a 30 minute period and the mixture then held at temperature for 1 hour. Then, 124 grams of propylene glycol monomethyl ether were added followed by 50.0 grams of diethylethanolamine. The reaction mixture was then cooled to 39°C. After cooling, 24.6 grams of propylenimine were added to the reactor and the reaction mixture then held at temperature for 2 hours. Following this hold period, 67.8 grams of diethylethanolamine were added to the reactor.

The resultant addition interpolymer had the following properties:

Solids content at 150°C.	51.7 percent
Gardner-Holdt viscosity	Z_8
Gardner color	5

The interpolymer of this example is water-thinnable and can also be thinned with an organic solvent such as ethyl Cellosolve.

EXAMPLE 11

This example illustrates the organic solvent and water-thinnable characteristics of the aminolysis-resistant addition interpolymers of the invention.

In this example, an aminolysis-resistant addition interpolymer was prepared and one sample of the interpolymer was thinned with an organic solvent and a second sample of the interpolymer was thinned with water.

The aminolysis-resistant addition interpolymer was prepared in the following manner:

Into a reactor equipped as in Example 1 was charged 312.3 grams of ethyl Cellosolve, 312.3 grams of dipropylene glycol monomethyl ether and 15.4 grams of water. The contents of the reactor were heated to reflux (about 125°C.) and a mixture consisting of 821.0 grams of isobutyl methacrylate, 352.0 grams of methacrylic acid, 35.0 grams of isooctyl thioglycolate, 64.0 grams of ethyl Cellosolve, 64.0 grams of dipropylene glycol monomethyl ether and 67.0 grams of tertiary-butyl peracetate was added over a 2 hour period and the reaction mixture held for about 1 hour. (Based on monomer solids, the monomer charge consisted of 70 percent isobutyl methacrylate and 30 percent methacrylic acid.) Following this hold period, 6.9 grams of tertiary-butyl peracetate, 13.0 grams of ethyl Cellosolve and 13.0 grams of dipropylene glycol monomethyl ether were added to the reaction mixture over a period of about 30 minutes. The reaction mixture was then held at temperature for about 1 hour. Then, 182.0 grams of ethyl Cellosolve and 182.0 grams of dipropylene glycol monomethyl ether were added to the reactor while the contents of the reactor were being cooled. While cooling was continuing, 294.0 grams of ethyl Cellosolve was added to the reaction mixture followed by the addition of 146.0 grams of diethylethanolamine. Then with the temperature of the reaction mixture at about 45°C., 68.9 grams of propylenimine were added to the reactor. The reaction mixture was then held at temperature for about 2.3 hours and 143.0 grams of diethylethanolamine and 140.0 grams of water were added to the reactor.

The resultant addition interpolymer had the following properties:

Solids content at 150°C,.	40.3 percent
Gardner-Holdt viscosity	Z^-
Gardner color	4

One sample of the above addition interpolymer was thinned with ethyl Cellosolve to produce an addition interpolymer product having a solids content at 150°C. of 35.6 percent.

A second sample of the above addition interpolymer was thinned with water to produce an addition interpolymer product having a solids content at 150°C. of 35.9 percent.

EXAMPLE 12

Into a reactor equipped as in Example 1 was charged 2624.0 grams of propylene glycol monomethyl ether. The contents of the reactor were heated to 118°C. and a mixture consisting of 3365.7 grams of isobutyl methacrylate, 1442.3 grams of methacrylic acid, 144.3 grams of isooctyl thioglycolate, 273.8 grams of tertiary-butyl peracetate and 524.8 grams of propylene glycol monomethyl ether was added over a 2 hour period (based on monomer solids, the charge contains 70 percent isobutyl methacrylate and 30 percent methacrylic acid). Then 28.0 grams of tertiary-butyl peracetate and 23.6 grams of propylene glycol monomethyl ether were added over a 30 minute period. Following this addition, 1573.5 grams of propylene glycol monomethyl ether were added to the reactor over a 30 minute period. The resultant addition interpolymer solution had a solids content measured at 150°C. of 52.3 percent, a Gardner-Holdt viscosity of Z2-Z3 and a Gardner color of 1.

To a 2 liter flask equipped with stirrer and thermometer were charged 1000.0 grams of the above addition interpolymer solution and 29.0 grams of propylenimine. The contents of the flask were held for 2 hours with stirring. Following this period, 94.1 grams of

pyridine were added to the flask. The resultant addition interpolymer salt had a solids content as measured at 150°C. of 49.8 percent. The interpolymer of this example is water-thinnable and can also be thinned with an organic solvent.

EXAMPLE 13

Into a reactor equipped as in Example 1 was charged 2624.0 grams of propylene glycol monomethyl ether. The contents of the reactor were heated to 118°C. and a mixture consisting of 3365.7 grams of isobutyl methacrylate, 1442.3 grams of methacrylic acid, 144.3 grams of isooctyl thioglycolate, 273.8 grams of tertiary-butyl peracetate and 524.8 grams of propylene glycol monomethyl ether was added over a 2 hour period (based on monomer solids, the charge contains 70 percent isobutyl methacrylate and 30 percent methacrylic acid). Then 28.0 grams of tertiary-butyl peracetate and 23.6 grams of propylene glycol monomethyl ether were added over a 30 minute period. Following this addition, 1573.3 grams of propylene glycol monomethyl ether were added to the reactor over a 30 minute period. The resultant addition interpolymer solution had a solids content measured at 150°C. of 52.3 percent, a Gardner-Holdt viscosity of Z2-Z3 and a Gardner color of 1.

Into a 2 liter flask was charged 1000 grams of the above addition interpolymer solution and 29.0 grams of propylenimine. The contents of the flask were then held for 2 hours with stirring. Following this period, 121.0 grams of N-methyl morpholine were added to the flask with stirring. The resultant addition interpolymer salt had a solids content as measured at 150°C. of 51.2 percent, a Gardner-Holdt viscosity of Z-10 and a Gardner color of 2. The addition interpolymer of this example is water-thinnable and can also be thinned with an organic solvent.

EXAMPLE 14

In this example, 20.0 grams of the addition interpolymer solution of Example 10 (prepared from monomer charged consisting of 70 percent cyclohexyl methacrylate and 30 percent methacrylic acid) was blended with 10.34 grams of Epon 828, a polyepoxide resin of epichlorohydrin-Bisphenol A having an epoxide equivalent of 185-192 and a viscosity as measured by ASTM D-445 of 100-160 passes, available from Shell Chemical Company.

The resultant composition was drawn down on a metal panel using a 3-mil Bird Bar. The coated panel was then permitted to air dry at ambient temperature for 24 hours and then was placed in a 140°F. oven for an additional 24 hours.

The cured and solvent resistance of the coating were evaluated utilizing the well-known acetone resistance test in which a cloth impregnated with acetone is rubbed across the surface of the film and the number of rubs needed to remove the film from the substrate is reported. The coating of this example resisted over 100 acetone rubs without any film loss or softening, indicating excellent cure and solvent resistance.

EXAMPLE 15

A coating composition was prepared by blending the following ingredients:

	Parts by Weight
Addition interpolymer solution of Example 12	690.0
Epon 834*	355.0
TiO_2	500.0
Silica (amorphous)	200.0
Propylene glycol monomethyl ether	88.0
Dipropylene glycol monomethyl ether	90.0
Igepal CO897**	30.0
H_2O	264.0

* An epoxy resin of epichlorohydrin-Bisphenol A having an epoxide equivalent of about 230-280 and a Gardner-Holdt viscosity of O-V, available from Shell Chemical Company.

** An emulsifier available from GAF Corporation.

EXAMPLE 16

A coating composition was prepared by blending the following ingredients:

	Parts by Weight
Addition interpolymer solution of Example 13	690.0
Epon 834	355.0
TiO_2	500.0
Silica (amorphous)	200.0
Propylene glycol monomethyl ether	88.0
Dipropylene glycol monomethyl ether	90.0
Igepal CO897	30.0
H_2O	264.0

EXAMPLE 17

Into a reactor equipped with a stirrer, thermometer, nitrogen inlet, dropping funnel and a condenser fitted with a water trap was charged 270.2 grams of propylene glycol monoethyl ether. The contents of the reactor were heated to 120°C. and a mixture consisting of 288.6 grams of isobornyl methacrylate, 123.7 grams of methacrylic acid, 12.4 grams of isooctyl thioglycolate, and 23.5 grams of tertiary-butyl peracetate was added over a 2 hour period. The reaction mixture was then held at temperature for one hour. (Based on monomer solids, the monomer charge consisted of 70 percent isobornyl methacrylate and 30 percent methacrylic acid.) After the hold period, 2.4 grams of tertiary-butyl peracetate and 12.1 grams of propylene glycol monomethyl ether were added to the reactor over a 30 minute period and the mixture then held at temperature for one hour. Then, 124.9 grams of propylene glycol monomethyl ether were added, followed by 50.0 grams of diethylethanolamine. The reaction mixture was then cooled to 39°C. After cooling, 24.6 grams of propylenimine were added to the reactor and the reaction mixture then held at temperature for two hours. Following this hold period, 67.8 grams of diethylethanolamine were added to the reactor.

The resultant addition interpolymer solution had a solids content measured at 150°C. of 51.7 percent, a Gardner-Holdt viscosity of Z-7, and a Gardner color of 12.

To 20.0 grams of this addition interpolymer solution were added 10.7 grams of Epon 828, an epoxy resin of epichlorohydrin-Bisphenol A having an epoxide equivalent of 185-192 and a viscosity as measured by ASTM D-445 of 100-160 poises, available from Shell Chemical Company.

The resultant polymeric composition was drawn down on a metal panel using a 3-mil Bird Bar. The coated panel was then permitted to air dry at ambient temperature for 24 hours and then was placed in a 140°F. room for an additional 24 hours.

The cure and solvent resistance of the coatings were evaluated utilizing the well-known acetone resistance test in which a cloth impregnated with acetone is rubbed across the surface of the film and the number of rubs needed to remove the film from the substrate is reported. The coating of this example resisted over 100 acetone rubs without any film loss or softening indicating excellent cure and solvent resistance.

EXAMPLE 18

Into a reactor equipped as in Example 1 was charged 270.2 grams of propylene glycol monoethyl ether. The contents of the reactor were heated to 120°C. and a mixture consisting of 288.6 grams of 2-ethylhexyl methacrylate, 123.7 grams of methacrylic acid, 12.4 grams of isooctyl thioglycolate, and 23.5 grams of tertiary butyl peracetate was added over a two hour period. The reaction mixture was then held at temperature for one hour. (Based on monomer solids, the monomer charge consisted of 70 percent 2-ethylhexyl methacrylate and 30 percent methacrylic acid.) After the hold period, 2.4 grams of tertiary-butyl peracetate and 12.1 grams of propylene glycol monomethyl ether were added to the reactor over a 30 minute period and the mixture then held at temperature for one hour. Then, 124.9 grams of propylene glycol monomethyl ether were added followed by 50.0 grams of diethylethanolamine. The reaction mixture was then cooled to 39°. After cooling, 24.6 grams of propylenimine were added to the reactor and the reaction mixture then held at temperature for two hours. Following this hold period, 67.8 grams of diethylethanolamine were added to the reactor.

The resultant addition interpolymer solution had a solids content measured at 150°C. of 51.7 percent, a Gardner-Holdt viscosity of Z-5 and a Gardner color of 3.

To 20.0 grams of the addition interpolymer solution were added 9.24 grams of Epon 828.

The resultant polymeric composition was drawn down, cured and tested for cure through and solvent resistance as in Example 17. The coating of this example resisted over 100 acetone rubs without film loss or softening, indicating excellent cure and solvent resistance.

WHAT WE CLAIM IS:

1. A two-package polymeric composition, the film-forming vehicle components of which comprise:
(a) a polyepoxide having a 1,2-epoxy equivalence of greater than 1.0 and a molecular weight below 4000; and
(b) an addition interpolymer which contains a polymeric backbone containing two or more interpolymerized ethylenically-unsaturated monomers, at least one of which contains carboxyl groups, and pendent thereto:
(1) anionic salt groups formed by reacting part of said carboxylic groups with a base, and
(2) amine groups formed by reacting part of said carboxyl groups with an alkylenimine;
said components (a) and (b) being inter-reactive to form a crosslinked, hard, solvent and stain-resistant material.

2. A polymeric composition as claimed in claim 1 in which said composition is water-reducible.

3. A polymeric composition as claimed in claim 1 in which either or both of said components (a) and (b) are in a solvent medium composed predominantly of water.

4. A polymeric composition as claimed in claim 3 in which any organic solvents present are water-miscible or water-reducible.

5. A polymeric composition as claimed in claim 1 in which said addition interpolymer has a pH greater than 7.0 in aqueous medium.

6. A polymeric composition as claimed in any one of claims 1 to 5 wherein said addition interpolymer is formed from a polymerizable alpha, beta-ethylenically unsaturated carboxylic acid and one or more other polymerizable ethylenically unsaturated monomers.

7. A polymeric composition as claimed in claim 6 wherein said carboxylic acid is acrylic acid or methacrylic acid, or a mixture thereof.

8. A polymeric composition as claimed in claim 6 or claim 7 wherein said carboxylic acid comprises from 5 to 95 percent by weight of said carboxylic acid and said other monomers.

9. A polymeric composition as claimed in any one of claims 6 to 8 wherein said other polmerizable ethylenically unsaturated monomer is an aminolysis-resistant organic monomer.

10. A polymeric composition as claimed in claim 9 wherein said aminolysis-resistant organic monomer is selected from mono-olefinic and diolefinic hydrocarbons, substituted or unsubstituted unsaturated carboxylic acid amides, unsaturated organonitriles, non-methyl esters of alpha, alkyl-substituted carboxylic acids and mixtures thereof.

11. A polymeric composition as claimed in claim 9 wherein the aminolysis-resistant organic monomer is a non-methyl ester of an alpha, alkyl-substituted carboxylic acid.

12. A polymeric composition as claimed in claim 11 wherein the aminolysis-resistant organic monomer is isobutyl methacrylate, cyclohexyl methacrylate or a mixture thereof.

13. A polymeric composition as claimed in any one of claims 1 to 8 wherein said alkylenimine is reacted with at least 15 mole percent of said carboxyl groups.

14. A polymeric composition as claimed in claim 13 wherein said alkylenimine is propylenimine or ethylenimine or a mixture thereof.

15. A polymeric composition as claimed in claim 1 wherein the anionic salt group is formed by reacting a part of said carboxyl groups with a sterically-hindered tertiary amine having the structure:

$$R_1 - \overset{\displaystyle R_2}{\overset{|}{N}} - R_3$$

wherein R_1, R_2 and R_3 are each aliphatic or cycloaliphatic radicals having from 2 to 10 carbon atoms.

16. A polymeric composition as claimed in claim 15 wherein the sterically-hindered amine is diethylethanolamine.

17. A polymeric composition as claimed in any one of claims 1 to 8, 13 and 14 wherein said polyepoxide resin is a polyglycidyl ether of a polyphenol.

18. A polymeric composition as claimed in claim 17 wherein said polyphenol is bisphenol A.

19. A polymeric composition as claimed in any one of claims 1 to 8, 13, 14, 17 and 18 wherein said vehicle components consist essentially of from 5 to 95 weight percent of said polyepoxide and from 95 to 5 weight percent of said addition interpolymer.

20. A composition as claimed in claim 1 and substantially as hereinbefore described with

reference to any one of Examples 1 to 6.

21. A composition as claimed in claim 1 and substantially as hereinbefore described with reference to any one of Examples 14 to 17.

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